FABRICATION AND CHARACTERIZATION OF CHITOSAN (CS) AND CHITOSAN (CS) BLENDED POLYVINYL ALCOHOL (PVA) MEMBRANE WITH POLYETHYLENE GLYCOL (PEG) 600 AS ADDITIVE

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A thesis submitted in fulfillment
of the requirements for the award of the degree of
Bachelor of Chemical Engineering (Biotechnology)

Faculty of Chemical and Natural Resources Engineering
Universiti Malaysia Pahang

MAY 2008

DECLARATION

"I declare that this thesis entitled '*Fabrication and Characterization of Chitosan (CS) and Chitosan (CS) Blended Polyvinyl Alcohol (PVA) Membrane with Polyethylene Glycol (PEG) 600 as Additive*' is the result of my own research except as cited in references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree."

Signature	:	……..……..
Name of Candidate	:	Rais Hanizam Madon
Date	:	16th May 2008

DEDICATION

Special Dedication to
Supiah Jamil@Jamin my beloved mother, you are everything to me,
Madon Jais my lated beloved father, you are my inspiration,
Rahemah Rahmat, I believe in you and me,

My family members that always love me,
My friends that always caring on me.

Thanks you for
always giving me encouragement towards this study.

ACKNOWLEDGEMENTS

In the Name of Allah, the Most Gracious, the Most Merciful.

I am so thankful to Allah S.W.T for giving me enough time, good health, spirit, and patient in order to complete this project research. With the mercifulness from Allah, therefore I can produce a lot of useful idea to this project.

I am also would like to express my thankfulness to my beloved family, especially my beloved mother, Mrs. Supiah Jamil@Jamin, for her prayers, support, patient, and guidance in my study.

I would like thank my supervisor, Mrs. Norashikin Mat Zain, for her continual professional advices, useful guidance, inspiration, patience and enormous support in the effort to complete this project.

I am indebted to Universiti Malaysia Pahang (UMP) for their facilities, opportunity as well as financial aid provided in pursuing my project research. I am also grateful to my panels, Mrs. Noor Ida Amalina Ahamad Nordin and Prof. Ir. Dr. Jailani Salihon for their brilliant idea, advice and guidance to me.

I would like to dedicate my appreciation to all the lecturer and associate of Faculty of Chemical and Natural Resources Engineering (UMP), that involve in this project for their invaluable time, guidance and advice. Without their cooperation and sacrifices, this research will not be able to complete and published.

Last but not least, I would also like to thank you to my lab partner, Junaidi Zakaria, Nuraini Mansor, and Winetta Arianty Ariffin who have accompanied me throughout this project. Thank you very much.

ABSTRACT

This research is about fabrication and characterization of flat sheet chitosan (CS) and chitosan (CS) blended polyvinyl alcohol (PVA) membrane with polyethylene glycol (PEG) 600 as additive. The main objective of this research is to fabricate high solute separation and flux membrane and also to determine the effect of PVA on membrane performance and morphology. The membrane were prepared by dry phase inversion method from casting solution containing PVA as polymer, CS as functional polymer, formic acid as solvent and PEG 600 as additive. The membranes were characterize in terms of pure water permeation (PWP), solute separation (R), flux (J) and membrane morphology by observation using scanning electron microscopy (SEM) and atomic force microscopy (AFM). The results for PWP, the membrane contain PVA obtained the highest PWP value because PVA give drastic effect in terms of hydrophilic. For the solute separation (R%) and flux (J), the membrane contains PVA yield the highest value for both characterization. This is because the PEG help to form pores for the membrane. By SEM observation found that the membrane that contain PVA give clearly view of pores. This contributes to high flux and pure water permeation. Lastly, by AFM analysis, it shows that the roughness parameter of membrane was effected by the PVA concentration. The membrane contains PVA show more rough surface because the nodules is not merge. From this research, can be conclude that PVA has become the solution to achieve both high selectivity and permeability in membrane.

ABSTRAK

Kajian ini dijalankan adalah untuk menghasilkan dan menganalisis sifat membran chitosan (CS) dan membran chitosan (CS) yang dikisar bersama dengan polyvynil alkohol (PVA) dan polyethylene glycol (PEG) 600 sebagai aditif. Objektif utama kajian ini adalah untuk menghasilkan membran yang mempunyai kadar penyingkiran bahan larut dan kadar fluks kemasukan air yang tinggi, dan juga untuk mengkaji kesan PVA ke atas prestasi dan bentuk fizikal membran. Membran tersebut telah dihasilkan melalui kaedah fasa penyongsangan yang kering, hasil daripada larutan Dope yang mengandungi PVA sebagai polimer, CS sebagai polimer berfungsi, asid formik sebagai pelarut dan PEG 600 sebagai aditif. Beberapa ciri-ciri membran telah dianalisis, iaini kadar kemasukan air tulen (PWP), kadar penyingkiran bahan larut, fluks kemasukan air, dan bentuk fizikal membrane yang di analisis menggunakan mikroskop pengimbas electron (SEM) dan mikroskop daya atom (AFM). Keputusan yang diperolehi untuk PWP, menunjukkan bahawa membran yang mengandungi PVA, memperolehi bacaan PWP terbesar. Ini adalah kerana PVA memberi kesan yang drastic kepada ciri ketelapan air. Beralih kepada kadar penyingkiran bahan larut dan fluks kemasukan air, membran yang mengandungi PVA menunjukkan bacaan data yang tinggi bagi kedua-dua ciri analisis tersebut. Ini adalah disebabkan bahawa PEG membantu dalam pembentukan liang di dalam membran tersebut. Daripada penilaian SEM, membran yang mengandungi PVA memberikan gambaran liang yang jelas. Hasilnya ialah, menyumbang kepada kadar fluks kemasukan air dan PWP yang tinggi. Akhir sekali, berdasarkan analisis AFM, menunjukkan bahawa parameter kekasaran membran dipengaruhi oleh kepekatan PVA. Membran yang mengandungi PVA mempunyai permukaan yang lebih kasar kerana bintil-bintil yang terhasil tidak bercantum antara satu sama lain.. Daripada kajian ini, dapat disimpulkan bahawa, PVA telah menjadi penyelesai masalah kepada pencapaian kadar ketelapan memilih dan kadar ketelapan kemasukan fluks.

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J	-	flux
V	-	volume
A	-	surface area
Δt	-	permeation time
X	-	distance
De	-	diffusion parameter
T	-	coagulation time
PWP	-	pure water permeation
Q	-	volume
R%	-	solute separation
C_p	-	concentration permeate
C_f	-	concentration retentate
wt%	-	weight percent for chemical per basis

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CHAPTER 1

INTRODUCTION

1.1 Background Study

1.1.1 Membrane Technology

Basically, membrane can be defined as a thin selective permeable layer which only permits mass transport pass through it based on pores size. Membrane also can be understand as a structure which is separating two phases and acting as an active or passive barrier to the transport of matter between the phases adjacent to it (Koops, 1995). For membrane processes, there is an interface, which is clearly materialized by a thin barrier that controls the exchange between two phases, not only by external forces and under the effect of fluid properties but also through the characteristics of the film material. Membrane separation process generally do not involve any phase changes because they are isothermal component which operate at room temperature (Drioli and Giorno, 1999). Norashikin (2006) had reported that the important goal in membrane technology is to control membrane structure, which affects the membrane performance. The most important characteristics of membrane is it selective transport properties. This selectivity properties is a combination of significant permeability with the intrinsic chemical properties of the materials forming the membrane and also the materials physical properties (Drioli and Giorno, 1999). Beside that, solubility and diffusivity of the penetrants in the dense polymeric phase, and the presence and size of micro pores or of electrical charge, play role in control the membrane transport phenomena. Asymmetric membranes is the most interesting for industrial application such as in reverse osmosis membrane, gas separation, ultrfiltration and microfiltration (Drioli and Giorno, 1999). This is because the

asymmetric membrane consists of a thin, dense layer in the top region over more macro porous supporting layer. The asymmetric structure can be obtained in a simple film by phase inversion or in composite systems by forming a thin dense layer. Tsai *et al*. (2006) had reported that for industrial use, need good separation of membranes and many polymer modification technologies have been applied to improve it.

1.1.2 Chitosan Membrane

Chitosan is an important biomass prepared by the deacetylation of chitin mainly obtained from crab and shrimp shell and is an aminopolysaccharide that is useful in chemical modifications because it has reactive amino and hydroxyl groups (Saxena *et al.,* 2006). Chitosan was chosen as the suitable membrane material because of its favorable permeaselectivity and solvent stability as well as good film forming properties (Feng *et al.,* 1996). Chitosan membrane show the impart of good hydrophilicity and excellent biocompatibility sequence cause of the original chitosan traits as the natural hidrophilicity biopolymer (Gabrovska *et al.,* 2007). Tsai *et al*. (2006) did investigated that chitosan is a good membrane material for Reverse Osmosis, Ultrafiltration and Microfiltration membrane. Wang *et al*. (2007) had reported that solid membrane, with chiral carrier or chiral derived polymer immobilized on it, is fairly stable and therefore a durable enantiomer separation process is possible. As for diffusion-selective membranes, enantiomer separation is achieved during membrane process through chiral environment within membrane. Chirality is a phenomenon which is of great importance to biological/chemical processes (Wang *et al*., 2007). Chitosan is diffusion selective (Wang *et al*., 2007) which consist a large quantity of chiral sites, and straightly exhibits excellent chiral selectivity (Kim *et al*., 2003).

1.2 Problem Statement

Membrane fouling is still a major problem in spite of much research devoted to its reduction or elimination (Hughes and Field, 2006). There is some reports are available stated that the chitosan has been used as a membrane forming material in preventing any membrane fouling, because of its hydrophilic nature and very high affinity for water. However, chitosan membranes are highly swollen in water and alcohol solutions, and the swollen membranes usually lose their permeaselectivity and show poor long-term stability of operation. In order to improve the stability and mechanical properties of chitosan based membranes, some solving method had been done such as bringing crosslinked structure to membranes, blending chitosan with other polymers like cellulose acetate and polyvinyl alcohol, casting chitosan on another polymer substrate to form composite membranes, and adding inorganic reinforcements into chitosan membranes (Saxena *et al.*, 2006).

A number of techniques such as copolymerization, blending, and crosslinking have been shown to be effective for improving pervaporation performance of the membranes (Jiraratananon *et a*l., 2002). Liu and Bai (2005) had reported that many commercial polymeric membrane materials, such as polysulfone (PS), polyethersulfone (PES), polyvinylidenedifluoride (PVDF), polypropylene (PP) and nylon, have good chemical, thermal and mechanical stability, but they are usually lack of reactive functional groups on the polymer backbones. Hence, membranes fabricated from these materials often have to be modified to eliminate the non-specific type of adsorption and to enhance the separation efficiency through improved adsorptive surfaces, especially for biomolecules such as proteins.

Compared with the above-mentioned materials, polyvinyl alcohol (PVA) and its derivatives are hydrophilic and have reactive hydroxyl groups (Jia *et al.*, 2007), which can be modified with other reactive functional groups to obtain adsorptive membranes. Among the various reactive functional groups such as hydroxyl group, amine group and sulfhydryl group, the amine groups or sulfhydryl groups are however much more reactive than the hydroxyl groups and can be used directly as affinity adsorption sites or can be much more easily attacked by other modifying

agents under mild conditions. Therefore, one of the choices to prepare adsorptive membranes can be to introduce some amine groups into PVA or its derivatives.

Yoshida and Kataoka (1989) had investigated that chitosan (CS), a biopolymer widely available from seafood processing waste, has been increasingly studied as an adsorptive material for various applications, due to its abundance in the free amine groups. Chitosan is an important biomass prepared by the deacetylation of chitin mainly obtained from crab and shrimp shell and is an aminopolysaccharide that is useful in chemical modifications because it has reactive amino and hydroxyl groups (Saxena *et al.,* 2006). There has been considerable research interest to prepare chitosan membranes (flat or preferably in hollow fiber form) for adsorptive separation purpose, but the scope of preparing pure chitosan membranes has been largely limited due to the poor mechanical strength and chemical stability of chitosan (Krajewska *et al*., 2001).

More recently, blending chitosan with other polymers has been found to be an effective way to overcome the shortcomings of chitosan, because blending at the microscopic level due to chemical interactions may form additional chemical bonds (Dufresne *et al*., 1999). Chitosan membranes blended with poly(vinyl alcohol) (PVA) have already been reported to have good mechanical properties because of the specific intermolecular interactions between PVA and chitosan in the blends (Koyano *et al*., 2000). Therefore, blending chitosan with other high strength polymers, for example PVA or its derivatives, is an attractive way to prepare adsorptive membranes for practical applications.

In this study, CS was blended with polyvinyl alcohol (CA) to form blend flat sheet membranes. PVA was used as the polymer matrix and CS as the functional polymer to provide amine groups for the flat sheet membrane in order to make it adsorptive. The choice of PVA as the polymer matrix is due to its long-known good mechanical strength in fabricating flat sheet. Formic acid was used as the co-solvent for CS and PVA to prepare the dope solution and sodium hydroxide (NaOH) solution was used in coagulant bath (Liu and Bai, 2005). Adsorptive membranes are attractive in many important separation applications such as removing heavy metal ions from

water or wastewater in environmental engineering, recovering proteins from fermentation broth in bioengineering and removing toxic substances from blood in hemodialysis.

Adsorptive membranes have reactive functional groups on the surfaces, including –COOH, –SO3H, and –NH2 groups, that can bond the targeted substances through specific interactions such as surface complexation or ion exchange. The adsorptive membranes have many unique advantages, including fast separation rates, high efficiency, good selectivity, low energy requirement and, possibly, large permeate flux (Han *et al.,* 2007). These materials provide an excellent binding capacity because chitosan molecules have both amino and hydroxyl groups that can be used to couple with ligands under mild conditions (Yang *et al*., 2002).

Beside that, many researchers have investigated the effect of different types of additives on membrane morphology and their performance. Arthanareeswaran *et al*. (2004) reported that concentration of additives greatly influenced the porosity and pore size of cellulose acetate membranes and their protein rejection studies revealed that the increase in additive concentration has direct influence on the permeate flux and rejection rates. Some researchers also reported that polyethylene glycol (PEG) was used to improve membrane selectivity being hydrophilic in character and as a pore forming agent (Shieh *et al*., 2001). Today's, the most challenging issues in membrane solid separation is the increasing of rejection rate and decreasing of flux rate. By doing this research of asymmetric flat sheet chitosan blended polyvinyl alcohol membrane and PEG as additives, can achieved both high selectivity and permeability of the membrane.

1.3 Objectives

The objectives of this research are listed as following.

i. To fabricate flat sheet chitosan membrane.
ii. To fabricate flat sheet chitosan blended polyvinyl alcohol membrane.
iii. To study the effect of polyvinyl alcohol (PVA) on chitosan membrane morphology.
iv. To study the effect of polyvinyl alcohol (PVA) on chitosan membrane performance.

1.4 Scopes of Research

The scopes of this research as follow.

i. Fabrication of chitosan membrane by using chitosan, formic acid and PEG 600.
ii. Fabrication of chitosan blended polyvinyl alcohol membrane by using chitosan, polyvinyl alcohol, formic acid and PEG 600
iii. Characterize the fabricated membrane using bovine serum albumin and lysozyme as solutes.
iv. Characterize the fabricated membrane morphology using scanning electron microscopy (SEM) and atomic force microscopy (AFM).

CHAPTER 2

LITERATURES REVIEW

2.1 Membrane History

For the last middle of 18th century, this membrane technology have been explore and studied but only to the basic phenomenon of separation and barrier properties rather in develop either for technical or industries uses (Mulder, 1996). The first commercial membranes for practical applications were manufactured by Sartorius in Germany after World War I which is come from the original idea of Zsigmondy (Mulder, 1996).

The development uses of membrane technology in industrial sector was achieved by the existence of asymmetric membranes (Loeb *et al*., 1962). Besides that, the phenomenon of dialysis had already known for long time, but the first practical membrane application on hemodialysis was demonstrated by Kolff in the 1940s (Kolff, 1944).

Reverse osmosis (RO) and nanofiltration (NF) have been used in drinking water production for almost 30 years, and they are increasingly applied in process water and wastewater treatments, particularly where the high quality of a product is desired (Koˇsuti´c *et al*., 2006).

Nowadays, the membrane science technology had an impressive growth for the last twenty years, confirming their potential to contribute to the solution of crucial problems of the world today and to sustainable industrial development. Table 2.1 show the development of technical membrane process (Mulder, 1996).

Table 2.1 : Development of technical membrane processes

Membrane Process	**Country**	**Year**	**Application**
Microfiltration	Germany	1920	Laboratory use (bacteria filter)
Ultrafiltration	Germany	1930	Laboratory use
Hemodialysis	Netherlands	1950	Artificial kidney
Electrodialysis	USA	1955	Desalination
Reverse osmosis	USA	1960	Sea water desalination
Ultrafiltration	USA	1960	Concentration of macromolecules
Gas separation	USA	1979	Hydrogen recovery
Membrane distillation	Germany	1981	Concentration of aqueous solutions
Pervaporation	Germany/Netherlands	1982	Dehydartion of organic solvents.

2.2 Overview of Membrane

2.2.1 Definition of Membrane

The increasing and broad interest in membrane operations results largely from their basic properties had already been observed and tested in biological systems. Membrane separation in general do not involves phase changes, they are athermal and work at room temperature. They are also non-destructive, because do not require the addition of others chemical (Drioli *et al*., 1999).

A membrane is a structure which separate two phases and acting as an active or passive barrier to the transport of matter between the phase adjacent to it (Koops, 1995). The basic membrane separation process as in Figure 2.1 (Mulder, 1996). A membrane can be thick or thin, its structure can be homogenous or heterogeneous, transport can be active or passive, passive transport can be driven by pressure, concentration or a temperature different (Mulder, 1996).

The most important characteristics of a membrane is its selective transport properties. Solubility and diffusivity of the penetrants in the dense polymeric phase, and the presence and size of micropores or of electrical charge, control the membrane transport phenomena (Drioli *et al*., 1999).

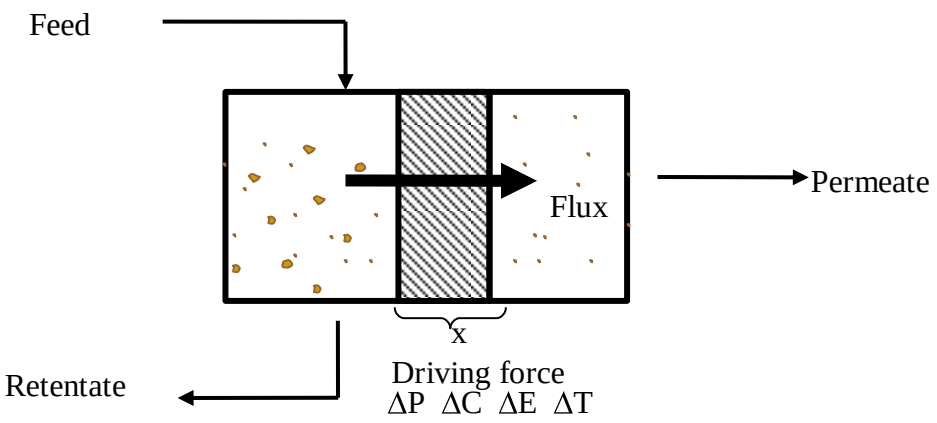

Figure 2.1 : Basic membrane separation process

2.2.2 The Advantages of Using Membrane Technologies

There is many advantages of using membrane technologies as listed below (Mulder, 1996).

i. Separation can be carried continuosly.
ii. Energy concumption is low.
iii. Easily to combine with other separation process (hybrid process).
iv. Separation can be carried out under mild conditions.
v. Up-scalling is easy.
vi. Membrane properties are variable and can be adjust.
vii. No additives requiremen in the process.

2.2.3 Membrane Process

The membrane has the ability to transport one component more readily than other because of differences in physical and chemical properties between the membranes and the permaring components (Mulder, 1996). The transport through membranes takes place as a result of a driving force acting on the components in the feed. The flux (*J*) of solute in membrane is obtained by this equation (Norashikin, 2006) :

$$J = \frac{V}{A \times \Delta t} \qquad (2.1)$$

Where,

V = volume of permeate (L)

A = membrane surface area (m^2)

Δt = permeation time (h)

2.2.4 Membrane Classification

For the membrane technology, can be classified into a few classes. The Table 2.2 show the classification of membrane (Drioli *et al*., 1999).

Table 2.2 : Production of membranes and application to various membranes processes.

Membrane class	**Method of preparation**	**Structure**	**Membrane process**
Symmetric microporous (dense polymer with cylindrical pores or capillaries-same pores and density structure)	• Stretching, hot and cold (PTFE) • Irradiation and track-etching • Casting and phase inversion (cellulose esters, polypropylene) • Molding and sintering (ceramics, polytetrafluoroethylene PTFE)	Random networks, pores 0.02-10μm diameter Parallel pores, 0.03-8μm. Random pores 0.1-1μm Random pores 0.1-20μm	Microfiltration Microfiltration Microfiltration, dialysis Microfiltration
Asymmetric Single component (membranes formed by a porous spongy wall supporting a very thin dense layer)	Casting and phase inversion (cellulosics, polyamides, polysulfone)	Dense or finely-porous skin grading of (macro) microporous substructure 0.5μm thick Pores range 0.001-0.2μm	Reverse osmosis, ultrafiltration, microfiltration, gas permeation
Composite	Film formation on microporous support	Dense skin on microporous sublayer	Reverse osmosis, gas permeation
Dynamic	Deposition of fine precoat on microporous barrier	Thin removable layer on microporous membrane	Reverse osmosis, ultrafiltration
Electrically charged	Sulfonation and amination of homogenous dense membrane.	Fixed charge groups in polymer matrix	Electrodialysis